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**ON THE RELEVANCE OF THE  
METHANE OXIDATION CYCLE TO "OZONE HOLE" CHEMISTRY**

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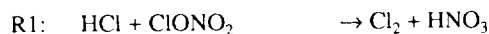
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**ABSTRACT**

High concentrations of active chlorine are clearly responsible for the observed ozone depletion during the Antarctic polar spring. However, the mechanism behind the activation of chlorine from the reservoir species HCl and ClONO<sub>2</sub> and the maintainance of extremely high levels of active chlorine after polar sunrise is less well understood. Here, we focus on the influence of the methane oxidation cycle on "ozone hole" chemistry through its effect on HO<sub>x</sub> and ClO<sub>x</sub> radicals. We demonstrate the great potential importance of the heterogeneous reaction HCl + HOCl → Cl<sub>2</sub> + H<sub>2</sub>O and the gasphase reaction ClO + CH<sub>3</sub>O<sub>2</sub> → ClOO + CH<sub>3</sub>O under sunlight conditions in polar spring. Under these conditions, the heterogeneous reaction is the main sink for HO<sub>x</sub> radicals. Through this channel, the HCl reservoir may be almost completely depleted. The gas phase reaction may control the levels of the CH<sub>3</sub>O<sub>2</sub> radical, provided that high levels of ClO exist. Otherwise this radical initiates a sequence of reactions leading to a considerable loss of active chlorine. Moreover, the production of HO<sub>x</sub> radicals is reduced, and thereby the efficiency of the heterogeneous reaction limited. The two reactions together may accomplish the complete conversion of HCl into active chlorine, thereby leading to a rapid destruction of ozone.

**1. INTRODUCTION**

It is now well-established that high levels of active chlorine are responsible for the observed depletion in stratospheric ozone in Antarctic polar spring. This is mainly accomplished through the ClO-dimer cycle (Molina and Molina, 1987; Anderson et al., 1991). The activation of chlorine through heterogenous reactions from the main reservoir species HCl is less well understood. Assuming that N<sub>2</sub>O<sub>5</sub> is largely converted to HNO<sub>3</sub> through heterogenous reaction on the background sulphate aerosol (Hanson and Ravishankara, 1991), then only the reaction

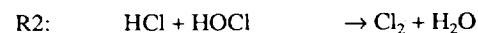


on nitric acid trihydrate (NAT) is known as a possible source of active chlorine *during* polar night. Thus ClONO<sub>2</sub> is titrated by HCl and a significant amount of gasphase HCl

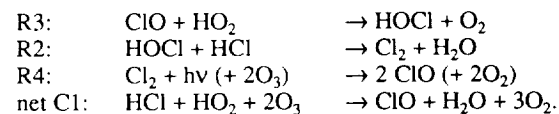
survives until sunrise after polar night. However, both high levels of observed ClO (Anderson et al., 1991) and very low HCl column amounts (Murcray et al., 1989; Toon et al., 1989) indicate, that most chlorine may already be in active form by the beginning of September in the lower stratosphere.

Both, ClONO<sub>2</sub> and HOCl (Hanson and Ravishankara, 1992; Abbatt and Molina, 1992) react rapidly with HCl on PSC surfaces, thus providing a channel for the fast removal of HCl. Therefore, in the presence of PSCs, ClONO<sub>2</sub> and HOCl should not be regarded as chlorine reservoirs. Rather, every ClONO<sub>2</sub> or HOCl molecule produced will react rapidly with HCl, thus providing a source of active chlorine.

However, ClONO<sub>2</sub> is an unlikely reaction partner since the necessary levels of ClONO<sub>2</sub> cannot be sustained as long as almost all of the active nitrogen is converted to HNO<sub>3</sub> and frozen out as NAT. Recently, Prather (1992) and Crutzen et al. (1992) have independently pointed out that the heterogeneous reaction



provides a much more efficient pathway for the completion of the liberation of the entire HCl reservoir after polar sunrise. Reaction R2 is efficient under sunlit conditions closing the reaction sequence (Crutzen et al., 1992)



For the very high ClO concentrations under "ozone hole" conditions, reaction R3 controls the HO<sub>2</sub> concentration; thus the net rate of cycle C1 may be expressed as:

$$-\frac{d(\text{HCl})}{dt} = \frac{d(\text{ClO}_x)}{dt} = P_{\text{OH}} \quad (1)$$

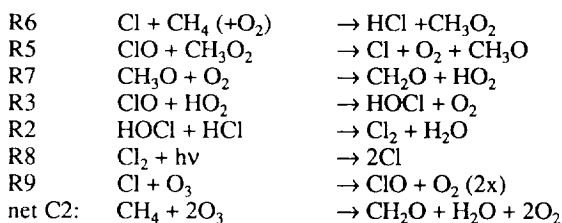
with P<sub>OH</sub> denoting the production rate of OH and HO<sub>2</sub> radicals.

## 2. METHANE OXIDATION AND "OZONE HOLE" CHEMISTRY

The methane oxidation cycle and "ozone hole" chemistry are closely linked because many compounds participating in the methane oxidation cycle react rapidly with the Cl radical. Moreover the reaction proposed by Simon et al. (1989)

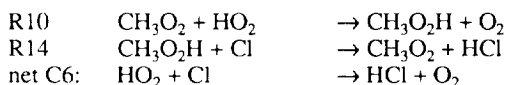
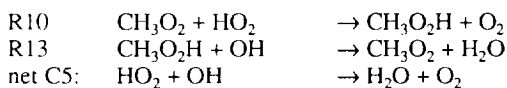
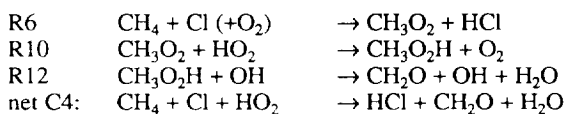
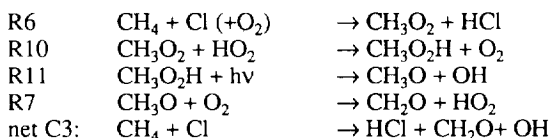


may constitute yet another link between these two systems. Crutzen et al. (1992) demonstrated that R5 strongly limits the effect of the deactivation of chlorine by formation of HCl through the reaction cycle:

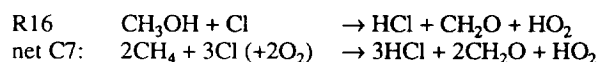
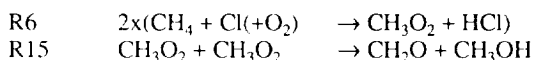


Under "ozone hole" conditions, R6 is the main source of  $\text{CH}_3\text{O}_2$  due to the high Cl concentrations.

Reaction R5 is relevant here because it closes cycle C2 and thereby largely controls the fate of the  $\text{CH}_3\text{O}_2$  radical. The latter would otherwise participate to a much larger extent in several cycles leading to a loss of both  $\text{HO}_x$  and active chlorine. Considering Eq. (1) it is clear that both the destruction of  $\text{HO}_x$  and the formation of HCl from Cl limit the amount of active chlorine under PSC conditions in Antarctic spring. Four parallel cycles are of importance under these conditions:

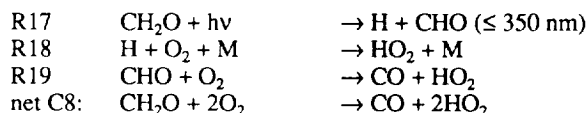


Moreover, the main channel for the  $\text{CH}_3\text{O}_2$  self-reaction at low temperatures (Horie et al., 1990) and the methanol oxidation should be considered



It is assumed for all these cycles, that gasphase  $\text{NO}_x$  concentrations are extremely low and Cl levels considerably elevated.

The photochemical breakdown of formaldehyde to carbon monoxide occurs along four pathways. One of these, takes place with a probability of about 40% and leads to the production of two  $\text{HO}_2$  radicals:



and thus strongly enhances cycle C1. Other channels for the decomposition of formaldehyde lead directly to the formation of CO without amplifying Cl.

## 3. MODEL RESULTS

Calculations were performed (see Crutzen et al., 1992, for details) for conditions at 75° S near 70 mb, starting on August 20, at about the time sunlight returns after the polar night, and continuing for 55 days. Initial chemical conditions, except ozone and water vapour concentrations, were taken from 2D model results for the beginning of the polar night but shifted downward by several kilometers to take into account a general downward motion in the polar vortex, indicated by  $\text{N}_2\text{O}$  measurements (Fahey et al., 1990). Dehydration as observed by Kelly et al. (1989) and a 75 % denitrification (Fahey et al., 1990) were taken into account. A linear increase in temperature (Fig. 1) was estimated from the measurements of Deshler and Hofmann (1991) at McMurdo station, 78° S, in 1990. Initial chemical conditions were:  $\text{O}_3$  1.6 ppmv (Deshler and Hofmann, 1991),  $\text{H}_2\text{O}$  2.2 ppmv (Kelly et al., 1989), HCl 1.6 ppbv,  $\text{ClONO}_2$  0.5 ppbv,  $\text{HNO}_3$  2.1 ppbv. Further additional assumptions were made:

- All  $\text{NO}_x$  gases, which were present at the onset of the polar night, were assumed to have been converted to  $\text{HNO}_3$  by reactions on sulphate aerosol particles before PSC formation, thus they did not affect the conversion of HCl to  $\text{ClO}_x$ .
- It was assumed that all  $\text{ClONO}_2$  and HOCl had reacted with HCl during the polar night on the NAT and ice particles to yield  $\text{Cl}_2$ . A reaction probability of  $\gamma = 0.3$  for R1 and  $\gamma = 0.2$  for R2 was adopted.
- Whenever temperatures were low enough for NAT existence (Hanson and Mauersberger, 1988)  $\text{HNO}_3$  was frozen out at a concentration of 1 particle/ $\text{cm}^3$ . The following calculations were performed:
  - Both reactions R2 and R5 were included.
  - Reaction R5 was not included, but reaction R2 was.
  - Reaction R2 was not included, but reaction R5 was.
  - Both reactions R2 and R5 were neglected.

Some results of the computer model runs on which this paper is based have already been discussed in Crutzen et al. (1992). The main findings are summarized in Fig. 1. Clearly in case D the HCl reservoir is not sufficiently

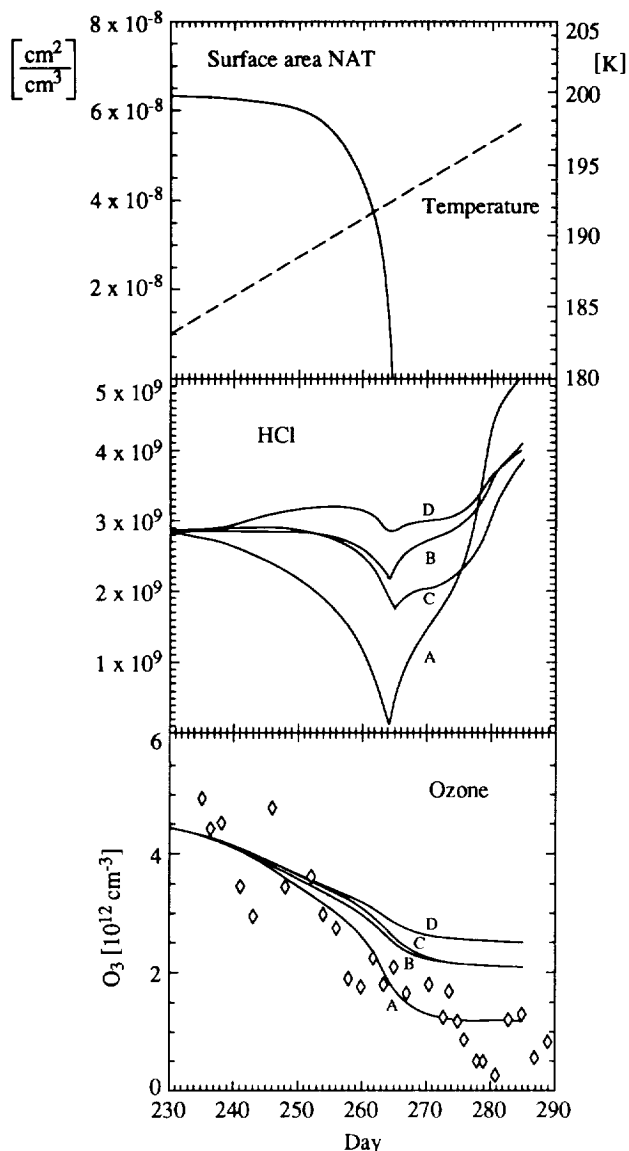


Fig. 1. The development of the surface area of NAT (in  $\text{cm}^2/\text{cm}^3$ ) and temperature, upper panel; the concentration of HCl (in molecules/ $\text{cm}^3$ ), middle panel and the ozone concentration (in molecules/ $\text{cm}^3$ ) over the model period. Daily variation of ozone and HCl are smoothed. Initial day is August 20, height 70 mbar. Diamonds indicate ozone measurements at approximately 70 mbar (Deshler and Hofmann, 1991). Line A shows results for reactions R2 and R5 included, line B with R5 neglected, line C with R2 neglected and line D with both R2 and R5 neglected. The last NAT particles evaporate around day 265 bringing an end to ozone depletion.

activated to reproduce the ozone destruction recorded in the measurements (Deshler and Hoffman, 1991). When either reaction R2 or R5 is included (case B and C respectively) the results improve. However, only when both R2 and R5 are introduced, does the model produce a strong depletion in both ozone and HCl.

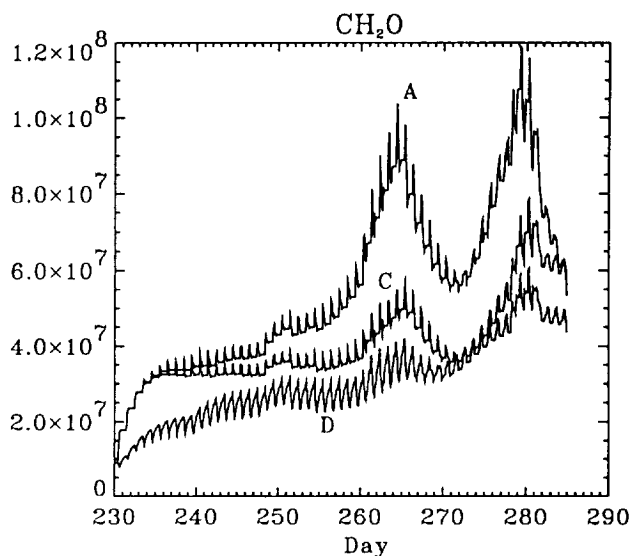


Fig. 2. The temporal evolution of the concentration of formaldehyde (in molecules/ $\text{cm}^3$ ) over the model period. Cases A, C, D are shown; case B (not shown) exhibits very similar, but slightly higher values than case D.

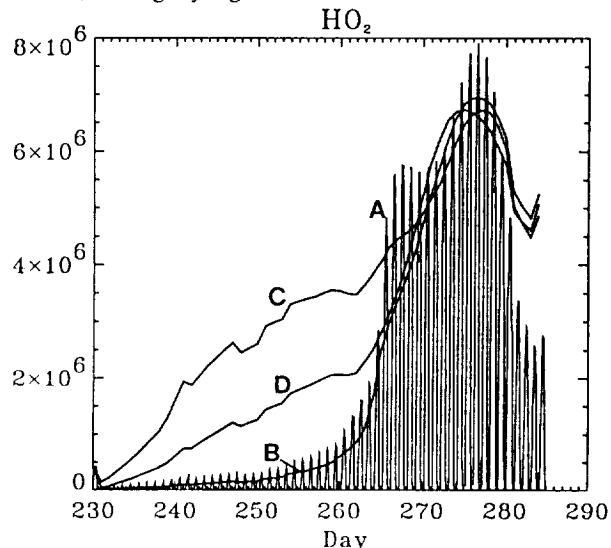


Fig. 3. As in Fig. 2, but for  $\text{HO}_2$  concentrations in molecules/ $\text{cm}^3$ . Case A shows diurnal variation, cases B, C, D only daily maximum values.

Fig. 2 shows the variation of formaldehyde over the model period. Compared to case D concentrations of  $\text{CH}_2\text{O}$  are about a factor of two higher, when both reactions R2 and R5 are included. The cause is an enhanced production through cycle C2. Reaction R5 is particularly efficient in enhancing the production of  $\text{CH}_2\text{O}$ , as can be seen from the higher concentrations in case A and C compared to case D (Fig. 2). High levels of  $\text{CH}_2\text{O}$  produce high concentrations of  $\text{HO}_x$  through cycle C8.

$\text{HO}_x$  radicals play a crucial role in the cycles discussed here. In Fig. 3, the efficiency of R2 in keeping  $\text{HO}_x$  at low levels (comp. A,B with D,C) under PSC conditions is evident. In case A, after the evaporation of the

NAT particles, a drastic increase in ClONO<sub>2</sub>, HOCl (Crutzen et al., 1992) and HO<sub>2</sub> (Fig. 3) was observed. The Cl radicals (Fig. 4) exhibit a distinct behaviour. As long as PSCs exist (until day 264) the buildup of active chlorine is reflected in an increasing concentration in Cl. From day 264 to 270 Cl decreases much like the ClO (Crutzen et al., 1992). However, from day 270 to 278 Cl increases again in contrast to ClO. During this period the ClO/Cl ratio is shifted in favour of Cl by the increase in NO by a factor of 20 from day 270 to 280. Prior to day 270, NO<sub>x</sub> (and thus NO) is kept at very low concentrations by the formation of ClONO<sub>2</sub> from ClO and NO<sub>2</sub> leading to the extremely high concentrations of ClONO<sub>2</sub> that peak around day 276. After day 278 Cl levels relax to background levels. High Cl concentrations enhance cycle C2 and thus HO<sub>x</sub> production. Therefore, the double peak structure for Cl is also apparent for CH<sub>2</sub>O (Fig. 2) and HO<sub>2</sub> (Fig. 3).

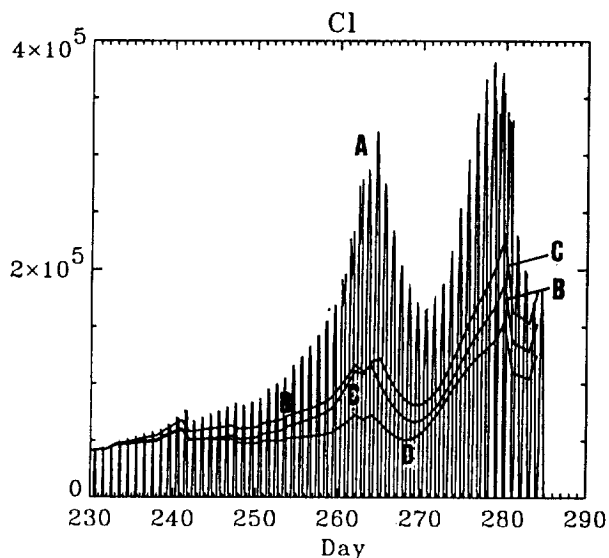


Fig. 4. As Fig. 3, but for Cl concentration in molecules/cm<sup>3</sup>. The extreme variability shown in case A represents the diurnal variation in Cl. For cases B, C and D only daily maximum values are shown.

## CONCLUSIONS

We have underlined the importance of reactions R2 and R5 in "ozone hole" chemistry. In particular, under sunlight conditions reaction R2 is the main source of active chlorine and indirectly, through cycle C1, the main sink of HO<sub>x</sub> as long as NAT surfaces are available to catalyse heterogeneous reactions. Also under these conditions, high levels of chlorine radicals lead to a significant replenishment of the HCl reservoir through reactions R6, R14, R16 and R21. However, reaction R5 would then control the levels of CH<sub>3</sub>O<sub>2</sub> through cycle C2 and thereby strongly reduce the efficiency of the reactions producing HCl. Moreover, in cycle C2 CH<sub>4</sub> is oxidized to CH<sub>2</sub>O without the loss of HO<sub>x</sub> radicals. In contrast, in the competing cycles C4, C5 and C6, HO<sub>x</sub> is lost. The decomposition of CH<sub>2</sub>O to CO however, constitutes a considerable source of HO<sub>x</sub>.

The drastic changes in ClONO<sub>2</sub>, HOCl, HCl, CH<sub>2</sub>O and HO<sub>2</sub> after evaporation of NAT predicted by the inclusion of reactions R2 and R5 should offer a focus for testing our theory. We therefore recommend both further investigation of the rate coefficients of R2 and R5 and atmospheric observations of the afore mentioned trace substances.

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